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DURING X-RAY IRRADIATION

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by

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The effect of various factors on the kinetics of the thermal decomposition of ammonium perchlorate has been investigated by several authors (for instance, see references [1,2]).

We obtained data on the effect of x-ray irradiation at the moment of decomposition on the kinetics of the decomposition of pure ammonium perchlorate and of ammonium perchlorate containing additives of solid inorganic semiconductors.

EXPERIMENTAL PART

In our tests we used a recrystalized preparation of "pure" quality. The samples were made by pressing at a pressure of 5 tons/cm^2 of the initial substance, carefully ground in a mortar, into tablets with a diameter of 5 mm and 18-20 mg. The additives were introduced to the original substance in the form of a fine powder prior to pulverization. The source of radiation was a RUP-200-20-5 x-ray instrument with a 3-BTN 200 tube. The radiation dose at the location of the sample was 300 r/min. We investigated the effect of preliminary irradiation and of irradiation at the moment of decomposition on the rate of thermal decomposition of perchlorate, both pure and containing 5% by weight of the additive, by the volumetric method on the apparatus and by the procedures outlined earlier [3]. It was established that irradiation for 45 minutes at the moment of decomposition has no effect on the decomposition of pure ammonium perchlorate (Fig. 1), and of samples of ammonium perchlorate containing 5% CdO, Fe_2O_3, CdS, WO_3, CuI,

PbO and MoO_2. During the time of irradiation at the moment of decomposition, the decomposition of ammonium perchlorate containing Ni_2O_3, NiO and Co_3O_4 in the very same quantities accelerates. As an example, data on the decomposition of ammonium perchlorate containing PbO and Ni_2O_3 are given in Figure 2. At the same radiation dosage, preliminary 30-minute irradiation of samples of ammonium perchlorate with additives, as in the case of pure ammonium perchlorate, accelerates its subsequent thermal decomposition (Figs. 1 and 2, curve 1). In this case the preliminary irradiation causes the acceleration of the decomposition both of the original, and of the partially decomposed pure ammonium perchlorate (Fig. 3).

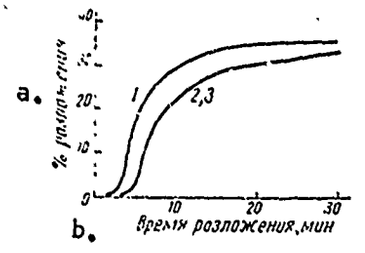

Figure 1. Thermal decomposition of pure ammonium perchlorate preliminarily irradiated for 30 minutes (1)., irradiated at the moment of decompostition (2), and not irradiated (3), at 272°C.

a. Percent decomposition
b. Time of decompostition, in minutes

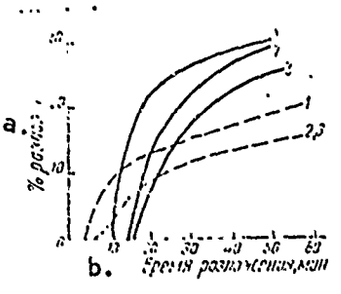

Figure 2. Thermal decomposition of ammonium perchlorate containing 5% Ni_2O_3 by weight (solid curves) and PbO (broken curves), preliminarily irradiated for 30 minutes (1), irradiated at the moment of decomposition (2), and not irradiated (3). The temperatures fo decomposition are 233°C. and 272°C. respectively.

a. Percent decomposition
b. Time of decomposition in minutes

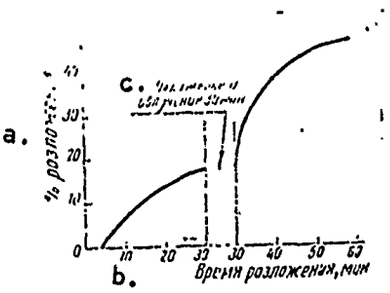

Figure 3. Effect of irradiation on the decomposition of partially decomposed pure ammonium perchlorate.

a. Percent of decomposition
b. Time of decomposition in minutes
c. Cooling and irradiation, 30 minutes

The study of the effect of the temperature at which preliminary irradiation was conducted on the acceleration of the subsequent thermal decomposition of ammonium perchlorate indicated that when the radiation doses are equal, a change in the temperature of preliminary irradiation from -28° C to +160° C, both in the case of pure ammonium chlorate and in the case of ammonium perchlorate containing additives of Ni_2O_3, NiO, and Co_3O_4, does not alter the kinetics of the subsequent thermal decomposition.[1]

Potentiometric determination in the irradiated samples of chloride and chlorate ions, which are the basic radiolysis products of ammonium chlorate [4], indicated that during irradiation by identical dosages (irradiation for 60 minutes at a dose of 1,000 r/min), the percent of the radialyzed pure ammonium perchlorate does not change as the irradiation temperature changes from -20° C to +150° C. In the presence of 5% additives of Ni_2O_3, Co_2O_3, NiO, Fe_2O_3 and PbO, the percent of the radialyzed ammonium perchlorate increases as the temperature rises. This effect is most pronounced in samples containing Ni_2O_3. The separate determination of Cl^- and ClO_3^- indicated that the increase in the percent of radialysis is caused basically by processes which result in the accumulation of Cl^-. The concentration of ClO_3^- in this case does not change significantly. Figure 4 gives data on the radialysis

[1] The tests were conducted on a heat balance apparatus in a nitrogen atmosphere.

of pure ammonium perchlorate (curve 1) and of ammonium perchlorate containing Ni_2O_3 (curve 2) at various temperatures; curve 3 corresponds to the percent of ammonium perchlorate with the additive Ni_2O_3, radialyzed with the liberation of ClO_3^-.

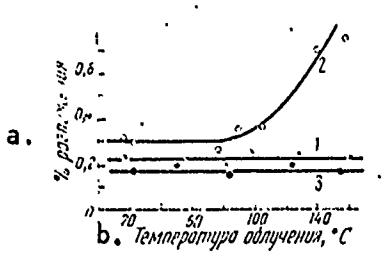

Figure 4. Temperature dependence of the radialysis of NH_4ClO_4 (explanation in text).

a. Percent of decomposition
b. Temperature of irradiation, °C

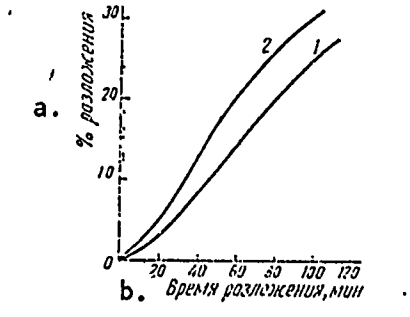

Figure 5. Effect of irradiation on the catalytic properties of Ni_2O_3 (1 - catalyzer not irradiated; 2 - catalyzer irradiated prior to mixing).

a. Percent of decomposition
b. Time of decomposition in minutes

The test on the decomposition of ammonium perchlorate containing NH_4Cl, which was introduced into the original substance in the quantity of 0.6 mol percent by cocrystallization from solution, indicated that the presence of

Cl^- retards the decomposition process.

Furthermore, it was determined that the irradiation of Ni_2O_3 by a dose of $2 \cdot 10^5$r results in increased catalytic activity in relation to the process of the thermal decomposition of ammonium perchlorate (Fig. 5).

DISCUSSION OF RESULTS

The mechanism of the effect of irradiation at the moment of decomposition on the rate of the process can be compared to the mechanism of the effect of preliminary irradiation on the rate of subsequent thermal decomposition, which usually is associated with stable, and sometimes irreversible, physical or chemical changes which occur in the substance under the effect of irradiation. The difference in the given case will be in that, first of all, at the moment of decomposition, irradiation takes place at a higher temperature, and secondly, the irradiation dosage received by the substance prior to the beginning of decompositon will be less than during the preliminary irradiation. On the other hand, during irradiation at the moment of decomposition, reversible changes which take place in a substance located in a radiation field, and which are characterized by a short lifetime, can have an effect on the kinetics.

Acceleration of the thermal decompostion of ammonium perchlorate by preliminary irradiation is related to the accumulation in the original substance of ClO_3^-, which is formed during the radialysis of ammonium perchlorate [5, 6]. From this point of view, the absence of the effect of the temperature of preliminary irradiation on the acceleration of the subsequent thermal decomposition can be related to the constant concentration of ClO_3^- in samples of ammonium perchlorate irradiated by equal dosages at various temperatures (Fig. 4, curve 3).

If we assume that the mechanism of the effect of irradiation at the moment of decompositon is similar to that of the effect of preliminary irradiation, then the absence of the effect of irradiation at the moment of decomposition on the rate of decomposition of pure ammonium perchlorate can be explained by the fact that the quantity of ClO_3^- accumulated in the irradiated sample by the moment of the beginning of decomposition is small and cannot have a great effect on the rate of decomposition. However, in this case it remains unclear why the accelerating action of irradiation does not show up by the end of the irradiation, when the dose received by the sample becomes quite high, while,as seen from Figure 3, the decomposition of partially decomposed ammonium perchlorate is accelerated by irradiation.

Furthermore, from this same point of view, we should assume that the additives of Ni_2O_3, Co_3O_4, and NiO greatly accelerate the formation of ClO_3^- due to radialysis, at least at higher temperatures, which insures the accumulation of ClO_3^- in quantities that can affect the decomposition process at doses much smaller than those received by the sample during preliminary irradiation. But analytical data indicate that the concentration of ClO_3^- in irradiated samples of ammonium perchlorate with these additives is less than in pure ammonium perchlorate, and does not change significantly as the irradiation temperature increases (for a sample with an additive of Ni_2O_3, see Fig. 4, curve 3). But at higher temperatures and in the presence of Ni_2O_3, the appearance of an extra quantity of Cl^-, which can be attributed to the slow thermal decomposition of the original substances at temperatures below the temperature of decomposition due to the catalytic effect of Ni_2O_3, can only retard the process.

Thus, the mechanism proposed for explaining the effect of preliminary irradiation on the rate of subsequent thermal decomposition of ammonium perchlorate does not completely explain the effects that take place during its decomposition in a radiation field. Apparently, in this case there are other changes at work, which are caused by irradiation in solid bodies, and whose effect on the decomposition process changes in the presence of additives of certain substances. Furthermore, we must consider the possibility of the change of catalytic activity of the additive under the effect of irradiation.

CONCLUSIONS

1. It has been established that irradiation at the moment of decomposition accelerates the decomposition of ammonium perchlorate containing additives of NiO, Ni_2O_3, and Co_3O_4, and has no effect on the kinetics of the decomposition of pure ammonium perchlorate and of ammonium perchlorate containing additives of CdO, CdS, Fe_2O_3, CuI, PbO, WO_3, MoO_2.

2. It has been shown that the existing theories on the mechanism of the effect of preliminary irradiation on the subsequent thermal decomposition of ammonium perchlorate do not explain the observed effect.

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13. ABSTRACT

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→ The article establishes that irradiation at the moment of decomposition accelerates the decomposition of ammonium perchlorate containing additives of NiO, Ni_2O_3, and Co_3O_4, and has no effect on the kinetics of the decomposition of pure ammonium perchlorate and of ammonium perchlorate containing additives of CdO, CdS, Fe_2O_3, CuI, PbO, WO_3, and MoO_2.

It has also been shown that the existing theories on the mechanism of the effect of preliminary irradiation on the subsequent thermal decomposition of ammonium perchlorate do not explain the observed effect.

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